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(21)Application number : 07-341580

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(54) LIQUID SEALING MATERIAL

(57)Abstract:

PROBLEM TO BE SOLVED: To obtain a liquid sealing material which can greatly improve the reliability of semiconductors in accelerated tests such as a pressure cracker test and a thermal shock test by using a specific composition.

SOLUTION: This liquid sealing material is composed of, as major components, (A) a liquid epoxy resin, (B) an alkylated diamino diphenyl methane which is a liquid aromatic amine hardener at room temp., (C) a polybutadiene compound having an epoxy group(s), (D) a silane coupling agent having not less than one functional group selected from among epoxy, amino and mercapto groups and an inorganic filler of which average particle size is 3-10μm and in which particles with their sizes of not more than 1μm account for 6-45wt.% and particles with their sizes of not less than 30μm account for not more than 25wt.% respectively of the total inorganic filler component, and the blending weight ratio of each component is given in the formula. ratios.

(c) / { (a) + (b) } (c)] − 0. 03 ~ 0. 20, (d) / { (a) + (b) + (c) } − 0. 02 ~ 0. 20 で、かつ (c) / { (a) ~ (b) + (c) − (d) + (c) } = 0. 60 ~ 0. 80

2 0.9:1 to 1.2:1 mole ratio
No solvent

AN 1997:521983 CAPLUS
DN 127:136836
ED Entered STN: 15 Aug 1997
TI Crack- and peeling-resistant liquid **epoxy resin sealing** materials for semiconductor packages
IN Kondo, Akihiro
PA Sumitomo Bakelite Co., Ltd., Japan
SO Jpn. Kokai Tokkyo Koho, 6 pp.
CODEN: JKXXAF
DT Patent
LA Japanese
IC ICM C08G059-56
ICS C08G059-56; C08K003-36; C08K005-54; C08L009-00; C08L063-00; C08L063-08; H01L023-29; H01L023-31
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PI JP 09176294	A2	19970708	JP 1995-341580	19951227
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PRAI JP 1995-341580		19951227		

CLASS

PATENT NO.	CLASS	PATENT FAMILY CLASSIFICATION CODES
JP 09176294	ICM	C08G059-56
	ICS	C08G059-56; C08K003-36; C08K005-54; C08L009-00; C08L063-00; C08L063-08; H01L023-29; H01L023-31

AB Title materials contain (a) liquid **epoxy resins**, (b) liquid alkylated diaminodiphenylmethane curing agents, (c) 0.30-0.10 [to (a + b)] epoxy-containing polybutadienes, (d) 0.02-0.10 [to (a + b + c)] silane coupling agents containing ≥1 functional groups chosen from epoxy, NH2, and SH, and (e) 0.50-0.80 [to (a + b + c + d + e)] inorg. fillers having following particle size distribution: average diameter 3-10 μm, ≤1 μm particle content 6-45%, ≥30 μm particle content ≤25%. Thus, bisphenol F diglycidyl ether **epoxy resin** 100, alkylated diaminodiphenylmethane 42, polybutadiene rubber 5, glycidyltrimethoxysilane 6, carbon black 1, and molten silica (average particle size 5.4 μm, ≤1 μm particle content 30%, 1-30 μm particle content 55%, ≥30 μm particle content 15%) 350 parts were mixed to prepare a semiconductor package showing peeling and crack resistance in a pressure cooker test and a thermal shock test.

ST **epoxy resin sealing** semiconductor package; crack resistant **epoxy resin sealing**; peeling resistant **epoxy resin sealing**; aminophenylmethane curing agent **epoxy resin**; polybutadiene **epoxy resin sealing** semiconductor; silane coupling agent **epoxy resin**; silica filler **epoxy resin sealing**

IT Crosslinking agents
(alkylated diaminodiphenylmethanes; crack- and peeling-resistant liquid **epoxy resin sealing** materials for semiconductor packages)

IT **Epoxy resins**, uses
RL: DEV (Device component use); POF (Polymer in formulation); PRP (Properties); USES (Uses)
(bisphenol F-based; crack- and peeling-resistant liquid **epoxy resin sealing** materials for semiconductor packages)

IT Electronic packaging materials
Fillers
Semiconductor devices
(crack- and peeling-resistant liquid **epoxy resin sealing** materials for semiconductor packages)

IT Butadiene rubber, uses

DERWENT-ACC-NO: 1997-399606

DERWENT-WEEK: 200112

TITLE: Liquid sealing material for semiconductors- containing epoxy! resin, alkylated di:amino:di:phenylmethane curative, polybutadiene containing epoxy group silane coupling agent and filler

PATENT-ASSIGNEE: SUMITOMO BAKELITE CO LTD[SUMB]

PRIORITY-DATA: 1995JP-0341580 (December 27, 1995).

PATENT-FAMILY:

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JP 09176294 A	July 8, 1997	N/A	006	C08G 059/56
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INT-CL (IPC): C08G059/50, C08G059/56 , C08K003/36 , C08K005/54 , C08K013/02 , C08L009/00 , C08L063/00 , C08L063/08 , H01L023/29 , H01L023/31 , C08K003:00 , C08K005:541 , C08K013/02

ABSTRACTED-PUB-NO: JP 09176294A

BASIC-ABSTRACT:

A liquid sealing material contains (A) a liquid epoxy resin, (b) a liquid alkylated diaminodiphenylmethane as aromatic amine curing agent, (c) polybutadiene compound having epoxy group, (d) a silne coupling agent having epoxy group, amino group and/or mercapto group as functional group and (e) inorganic filler having specific distribution of particle size. The weight ratio of (c)/((a)+(b)+(c)) is 0.0.03-0.10, (d)/((a)+(b)+(c)) is 0.02-0.10 and (e)/((a)+(b)+(c)+(d)+(e)) is 0.50-0.80.

USE - The material is suitable for sealing a semiconductor.

ADVANTAGE - The sealing material has high reliability without peeling and cracking on pressure cooker test or a thermal test.

CHOSEN-DRAWING: Dwg.0/0

TITLE-TERMS: LIQUID SEAL MATERIAL SEMICONDUCTOR CONTAIN POLYEPOXIDE RESIN ALKYLATED DI AMINO DI PHENYLMETHANE CURE POLYBUTADIENE CONTAIN EPOXY GROUP SILANE COUPLE AGENT FILL

DERWENT-CLASS: A12 A21 A85 E19 L03 U11

CPI-CODES: A05-A01E2; A08-D03; A08-M01; A08-R01; A12-E04; A12-E07C; E05-E01; E05-E02; E05-E03; E10-B01A4; E31-P03; L04-C20A;

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CHEMICAL-CODES:
Chemical Indexing M3 *01*
Fragmentation Code
G011 G012 G013 G014 G015 G016 G017 G018 G019 G100

* NOTICES *

1.This document has been translated by computer. So the translation may not reflect the original precisely.
2.**** shows the word which can not be translated.
3.In the drawings, any words are not translated.

DETAILED DESCRIPTION

[Detailed Description of the Invention]
[0001]
[Field of the Invention] This invention relates to the liquefied closure ingredient used for the closure of a semi-conductor.
[0002]
[Description of the Prior Art] Although the liquefied closure ingredient was used for the plastics pin grid array (henceforth PPGA) mold semi-conductor closure, compared with the hermetic seal mold by the ceramics, it was not enough in respect of dependability, and the spread of plastic packages was behind compared with the dual in-line (henceforth DIP) mold. As a cause of a dependability fall of a PPGA mold semi-conductor, moisture invades from the organic printed-circuit board by which [** package processing was carried out. ** In order unlike transfer mold shaping of a DIP mold package to flow in a package and to fabricate a liquefied closure ingredient by the non-draft, when air bubbles remain and heat stress is added into resin, a crack occurs. ** Since the coefficient of linear expansion of resin, and a semiconductor chip and an organic substrate differs, when heat stress is added, exfoliation by the interface will be produced and invasion of moisture will be made easy.] ** is mentioned.
[0003]
[Problem(s) to be Solved by the Invention] This invention offers the liquefied closure ingredient which can improve the dependability of a semi-conductor sharply also in accelerated tests, such as a pressure cooker test (henceforth PCT), and a cold energy cycle test (henceforth traveler's check).
[0004]
[Means for Solving the Problem] Then, the result to which examination was wholeheartedly come in piles in order that this invention might solve such a conventional problem, The aromatic amine system curing agent alkylation diamino diphenylmethane which is a liquid in a liquefied epoxy resin and ordinary temperature, To the polybutadiene compound and silane coupling agent which have an epoxy group The constituent which blended the inorganic filler which has specific particle size distribution A pressure cooker test (It is hereafter called PCT) It finds out becoming the closure ingredient which can improve the dependability of a semi-conductor sharply also in accelerated tests, such as a cold energy cycle test (henceforth traveler's check), and comes to complete this invention. Namely, the aromatic amine system curing agent alkylation diamino diphenylmethane whose this invention is a liquid in (a) liquefied epoxy resin and (b) ordinary temperature, (c) The polybutadiene compound, the (d) epoxy group which have an epoxy group, In the liquefied closure ingredient which uses as a principal component the silane coupling agent which has in intramolecular an amino group and one or more functional groups chosen from the group of a sulfhydryl group, and the inorganic filler which has the particle size distribution of (e) specification The blending ratio of coal of each component by the weight ratio by (c)/{(a)+(b)+(c)} =0.03-0.10 and (d)/{(a)+(b)+(c)} =0.02-0.10 And it is (e)/{(a)+(b)+(c)+(d)+(e)} =0.50-0.80, and the mean particle diameter of the inorganic filler of (e) is 3-10 micrometers. A thing with a particle size of 1 micrometer or less is 6 - 45 % of the weight among [all] an inorganic filler component, and it is the liquefied closure ingredient which blended the inorganic filler with which

a thing with a particle size of 30 micrometers or more has 25 or less % of the weight of the particle size distribution in [all] an inorganic filler component. The dependability of the PPGA mold semi-conductor using an organic printed-circuit board can be raised sharply.

[0005]

[Embodiment of the Invention] As for the liquefied epoxy resin of (a) used for this invention, it is desirable 50% of the weight or more of the component of that the viscosity in 25 degrees C is below 10Pa and s. Since air bubbles are involved in, or it will become easy to generate the short shot to a corner edge and will lead to a dependability fall in case the viscosity of a constituent becomes high and carries out inflow closure of under a PPGA package with a liquefied closure ingredient if 50% of the weight or more of an epoxy resin component is not liquefied epoxy of hypoviscosity, it is not desirable. In the case of a liquefied ingredient, as a viscosity measuring method of an epoxy resin, it measures with E mold viscometer made from East Machine Industry in 25 degrees C at a room temperature. If it is the epoxy resin with which are satisfied of this requirement and an example will be given although not limited especially A bisphenol A diglycidyl ether mold epoxy resin, a bisphenol F diglycidyl ether mold epoxy resin, A bisphenol S diglycidyl ether mold epoxy resin, 3, 3', 5, 5'-tetramethyl - 4 4'-dihydroxybiphenyl-diglycidyl-ether mold epoxy resin, A 4 and 4'-dihydroxybiphenyl-diglycidyl-ether mold epoxy resin, There are 1, 6-dihydroxybiphenyl-diglycidyl-ether mold epoxy resin, a phenol novolak mold epoxy resin, a bromine mold cresol novolak mold epoxy resin, a bisphenol D diglycidyl ether mold epoxy resin, etc. These do not interfere, even if it mixes, even when it is independent. Moreover, in order to obtain the liquefied closure ingredient which was excellent in dependability, the fewest possible things of ionicity impurities, such as Na+ and Cl-, are desirable [the epoxy resin which is equal to use].

[0006] The aromatic amine system curing agent of (b) used for this invention is alkylation diamino diphenylmethane, and is the thing of a liquid in ordinary temperature. The amines which do not have a ring are lacking in thermal resistance, since they are rich in reactivity also under the ambient atmosphere below nullity, have the fatal fault of being inferior to shelf life, and are not suitable for this invention. Moreover, in order to obtain the liquefied closure ingredient which was excellent in dependability, the fewest possible things of ionicity impurities, such as Na+ and Cl-, are desirable [the amine system curing agent which is equal to use]. As for the aromatic amine system curing agent of (b), an ingredient with a very sufficient fluidity can be offered with combination with (a) liquefied epoxy resin. Even if it flows in a package and makes it harden by the non-draft, air bubbles all cannot generate fluid faults, such as a void and being un-filled up, easily, either. base resin -- it is -- (-- a --) -- an epoxy resin -- a curing agent -- it is -- (-- b --) -- aromatic amine -- a system -- a curing agent -- alkylation -- diamino -- diphenylmethane -- combination -- a mole ratio -- {-- (-- a --) -- /-- (-- b --) --} -- 0.9-1.2 -- being desirable . When less than 0.9 curing agent is excessive, the superfluously unreacted amino group will remain and it leads to the fall of damp-proof fall and dependability. Conversely, if it exceeds 1.2 (i.e., if epoxy resins increase in number), hardening will become inadequate and it will lead to the fall of dependability.

[0007] As an elastomer used for this invention, compatibility with the epoxy resin of (a) is good, and the polybutadiene compound which has the epoxy group of (c) from which the reduction in stress and toughening are expected is mentioned. Generally, since an elastomer lacks in compatibility with an epoxy resin, after it carries out impregnation hardening, it has the property in which a moldability falls for bleeding. However, in order that compatibility may react in part with increase and a curing agent (b) and may construct a bridge by including an epoxy group in some molecules, bleeding nature becomes good and is considered that it can also discover the reduction in stress and toughening peculiar to polybutadiene which have an epoxy group. 1000-2000 have [the polybutadiene compound which has an epoxy group] desirable number average molecular weight. If it is less than 1000, it will become easy to carry out bleeding, if 2000 is exceeded, viscosity will become high, and it is not all desirable. Moreover, 3 - 10% of epoxy content (principal chain addition mole fraction %) is desirable. When it is less than 3%, compatibility is missing, if 10% is exceeded, a bridge will be constructed with a curing agent, and in order not to take the so-called sea island structure, it becomes impossible to desire low stress-ization.

Although for example, KIC measurement is mentioned to for example, a three-point bending test and the check of toughening at the check of the reduction in stress, the result of having excelled in any result of a test can be obtained. The polybutadiene compound which has this epoxy group can pull out low stress nature and toughness by adjusting that addition to the maximum extent. Although (c)/{(a)+(b)+(c)} =0.03-0.10 are desirable as for an addition, if it is less than 0.03, it cannot desire effectiveness of the reduction in stress, and toughening, and becomes the cause which a surface crack occurs especially at the time of traveler's check (heat cycle test), and leads to the defect of dependability. Moreover, if 0.10 is exceeded, compatibility with the epoxy resin of (a) will worsen and will cause an oil float and moldability fall of carrying out bleeding, on a package front face. Furthermore, you may combine with the polybutadiene compound which there is the low stress effectiveness and has the epoxy group of (c), a random copolymerization silicone modified epoxy resin with compatibility, random copolymerization silicone denaturation phenol resin, or the polyolefine of epoxy group content.

[0008] As a silane coupling agent which has in intramolecular the epoxy group of (d), an amino group, and one or more functional groups chosen from the group of a sulfhydryl group, an epoxy silane (for example, KBM[by Shin-Etsu Chemical Co., Ltd.]- 403) is desirable. Moreover, if needed, an amino silane and a mercapto silane may be twisted in part, and may be carried out to the coupling agent whole quantity, and you may all add to raise adhesion with a substrate according to an application.

[0009] As an inorganic filler (only henceforth a filler) of (e), a crystal silica, fused silica, etc. are used, for example. Although a configuration generally has the shape of a globular shape, the letter of crushing, and a flake etc., in order to attain reduction-ization of coefficient of linear expansion and to raise the effectiveness by adding more fillers, a spherical inorganic filler is the best. As for an addition, (e)/{(a)+(b)+(c)+(d)+(e)} =0.50-0.80 are desirable. When it is less than 0.50, the reduction effectiveness of an above-mentioned coefficient of linear expansion is small, and if 0.80 is exceeded, the viscosity of the liquefied closure ingredient obtained as a result will become high too much, and since it is not practical use level, it is not desirable. Moreover, it is possible by adjusting the particle size distribution of a filler to pull out flowability, such as viscosity, to the maximum extent. It is known that there is an inclination for viscosity to become low as the filler in which the filler which generally has the large particle size distribution of a range has a big particle size. However, although viscosity becomes low, the comparatively heavy filler of the filler which arranged only a big particle size of 50 micrometers or more for the purpose of hypoviscosity-izing of specific gravity is certainly depressed during hardening, and the so-called filler sedimentation from which a presentation ratio differs by the upper and lower sides of a hardened material occurs. Moreover, the point of not flowing into a slit is mentioned as a fault using a filler with a big particle size. It is in the inclination of the package of the formation of many pin-ized space-saving, and the pitch between wire wires is becoming narrow as an example recently so that it may be represented by the PPGA mold package. It is in such an inclination, a liquefied closure ingredient is flowed by the non-draft, and in order to fabricate so that there may be no fluid faults, such as a void and being un-filled up, particle size of a filler must be made small. However, the fault by which a fluidity is spoiled also increases by making particle size small. Then, a fluidity is not spoiled, either, when mean particle diameter of a filler is made smaller than 3-10 micrometers and that of the conventional liquefied closure ingredient and a thing with a particle size of 30 micrometers or more makes small 25 or less % of the weight and particle size in a solid-stowing material component. Moreover, a thing 1 micrometer or less can suppress sedimentation of the filler whose filler of a particle tends to be depressed by adjusting optimum dose ON ** and particle size distribution in 6 - 45 % of the weight, and the filler of a particle at the time of hardening among a solid-stowing material component. The particle size distribution and mean particle diameter as used in the field of this invention are measured by the laser formula (Horiba, LA-500). In addition, the mean diameter was taken as the median size. The liquefied closure ingredient ingredient of this invention is not hindered by **** for additives, such as the catalyst for promoting other resin and reactions other than the aforementioned indispensable component if needed, a diluent, a pigment, a coupling agent, a flame retarder, a leveling agent, and a defoaming agent,, either. With 3 rolls, a liquefied closure ingredient carries out distributed kneading, carries out bottom degassing processing of a vacuum, and manufactures for example, each

component, an additive, etc.
[0010]
[Example] The example and the example of a comparison which show this invention below explain.
- Bisphenol F diglycidyl ether mold epoxy resin: (weight per epoxy equivalent 155, 1.6 Pa-s / 25 degrees C) The 100 weight sections and naphthalene F diglycidyl ether mold epoxy resin: (135 or 124 or less Pa-s of equivalents, 25 degrees C)
- Alkylation diamino diphenylmethane curing agent: (amino equivalent 65) Polybutadiene rubber which has 42 weight sections and an epoxy group: Five weight sections (epoxy number-average-molecular-weight 1500 and content % of five mols)
- Glycidyl trimethoxysilane: Six weight sections and fused silica: The 350 weight sections and carbon black: Distributed kneading of the raw material of 1 weight section above was carried out with 3 rolls, bottom degassing processing of a vacuum was carried out, and the liquefied closure ingredient was obtained. Using the obtained liquefied closure ingredient, the PPGA package was closed, it hardened in 3-hour oven at 165 degrees C, and the semiconductor package was obtained.
[0011] <<evaluation approach>>
- Viscosity : what was measured by 2.5rpm with E mold viscometer (25 degrees C) was made into the value. It is so bad that this value is high. If viscosity exceeds 50Pa and s, the workability at the time of dispensing will worsen.
- CHIKISO ratio : the ratio of the viscosity in 0.5rpm and 2.5rpm was made into the value with the above-mentioned viscometer.
- Shelf life : the time amount which becomes one twice the viscosity of initial viscosity was taken.
O For 72 hours or more and **, 24 - 72 hours and x are 24 or less hour and hardenability :P The liquefied closure ingredient was poured into PGA package piece parts, it hardened in 165 degrees C of hardening conditions, and 3 hours, and the number of the voids on the front face of a package and filler separation were observed. The number of the voids on the front face of a package was observed under the microscope, and made the void several micrometers or more ****. The non-filling package was observed with the ultrasonic murder machine (it is called Following SAT). Filler separation ground the cross section of a package and measured the thickness of a surface resin layer. The thing 5 micrometers or more was expressed as those with filler separation. The number of the evaluated PPGA packages is ten.
- the exfoliation and crack ** processing after hardening -- exfoliation with a semiconductor chip and a printed circuit board interface and the existence of a crack were checked using SAT about the 720 hours after [before **PCT processing (125 degree-C/2.3atm)] **traveler's check processing (-65-degree-C / 30 minutes <- ->150 degrees C /, 30 minutes) 1000 cycle back. The number of the evaluated PPGA packages is ten.
[0012]
Table 1 Si Li Mosquito A B C D E F Mean particle diameter (micrometer) 5.4 4.2 7.8 2.5 3.2 7.3 Weight [of 1 micrometer or less] % 30 39 20 40 48 10 Weight % 55 [1-30-micrometer] 52 62 55 51 61 Weight [of 30 micrometers or more] % 15 9 18 5 1 29 [0013]
Table 2 Fruit ** Example 1 2 3 4 5 Combination (weight section)
Bisphenol female mold diglycidyl ether epoxy resin 100 100 100 100 60 Naphthalene mold diglycidyl ether epoxy resin 40 Alkylation diamino diphenylmethane 42 42 42 42 47 Polybutadiene rubber 5 5 5 5 5 Glycidyl trimethoxysilane 6 6 6 6 6 Carbon black 1 1 1 1 1 Fused silica A 350 500 350 Fused silica B 350 Fused silica C 350 Property Viscosity (Pa-s) 30 45 36 24 38 CHIKISO ratio 1.2 1.2 1.3 1.1 1.3 Shelf life O O OO O hardenability The number of voids 0 0 0 0 0 Non-filling 0 0 0 0 0 Filler separation Nothing Nothing Nothing Nothing Nothing After [hardening] exfoliation 0 0 0 0 0 A crack 0 0 0 0 0 After PCT processing Exfoliation 0 0 0 0 0 Crack 0 0 0 0 0 After [traveler's check processing] exfoliation 00 0 0 Zero crack 0 0 0 0 0 [0013]
Table 3 Ratio ** Example 1 2 3 4 5 Combination (weight section)
Bisphenol female mold diglycidyl ether epoxy resin 100 100 100 100 30 Naphthalene mold diglycidyl ether epoxy resin 70 Alkylation diamino diphenylmethane 42 42 42 42 45 Polybutadiene rubber 5 5 5 5

5 Glycidyl trimethoxysilane 6 6 6 6 6 Carbon black 1 1 1 1 1 Fused silica A 200 350 Fused silica D 350 Fused silica E 350 Fused silica F 350 Property Viscosity (Pa-s) 43 54 27 17 76 CHIKISO ratio 1.1 1.2 1.3 1.1 1.3 Shelf life O O OO x hardenability The number of voids 2 15 0 0 3 non-filling 1 2 0 0 20 Filler separation ** Nothing ** Nothing Nothing After hardening Exfoliation 0 0 0 0 0 A crack 0 0 0 0 0 After PCT processing Exfoliation 0 0 0 10 4 Crack 0 0 0 6 2 After [traveler's check processing] exfoliation 0 0 0 10 0 Crack 0 0 0 10 0 [0014]

[Effect of the Invention] If the liquefied closure ingredient of this invention performs the closure of a semiconductor package, since it will come out to obtain the semi-conductor of the high-reliability which does not have an exfoliation crack in a pressure cooker test or a cold energy cycle test, it is industrial merit size.

[Translation done.]

* NOTICES *

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2.**** shows the word which can not be translated.
3.In the drawings, any words are not translated.

CLAIMS

[Claim(s)]
[Claim 1] (a) The aromatic amine system curing agent alkylation diamino diphenylmethane which is a liquid in liquefied epoxy resin and (b) ordinary temperature, (c) The polybutadiene compound, the (d) epoxy group which have an epoxy group, In the silane coupling agent which has in intramolecular an amino group and one or more functional groups chosen from the group of a sulfhydryl group, and the liquefied closure ingredient which uses as a principal component the inorganic filler which has the specific particle size distribution which show (e) following The blending ratio of coal of each component by the weight ratio by (c)/{(a)+(b)+(c)} =0.03-0.10 and (d)/{(a)+(b)+(c)} =0.02-0.10 And the liquefied closure ingredient characterized by being (e)/{(a)+(b)+(c)+(d)+(e)} =0.50-0.80.
[Claim 2] (e) Liquefied closure ingredient according to claim 1 with which mean particle diameter is as follows [particle-size 1micrometer] 6 - 45 % of the weight among [all] an inorganic filler component in 3-10 micrometers for an inorganic filler, and a thing with a particle size of 30 micrometers or more has 25 or less % of the weight of the particle size distribution in [all] an inorganic filler component.

[Translation done.]

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(54)【発明の名称】　液状封止材料

(57)【要約】

【課題】　プレッシャークッカーテストや冷熱サイクルテストにおいても剥離クラックのない高信頼性の半導体パッケージ用の液状封止材料を提供する。

【解決手段】　（ａ）液状エポキシ樹脂、（ｂ）常温で液体である芳香族アミン系硬化剤アルキル化ジアミノジフェニルメタン、（ｃ）エポキシ基を有するポリブタジエン化合物、（ｄ）エポキシ基、アミノ基、メルカプト基の群から選ばれる１個以上の官能基を分子内に有するシランカップリング剤、及び（ｅ）特定の粒度分布を有する無機充填材を主成分とする液状封止材料において、各成分の配合割合が重量比で（ｃ）／｛（ａ）＋（ｂ）＋（ｃ）｝＝０．０３～０．１０、（ｄ）／｛（ａ）＋（ｂ）＋（ｃ）｝＝０．０２～０．１０で、かつ（ｅ）／｛（ａ）＋（ｂ）＋（ｃ）＋（ｄ）＋（ｅ）｝＝０．５０～０．８０である液状封止材料。

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【特許請求の範囲】

【請求項1】（a）液状エポキシ樹脂、（b）常温で液体である芳香族アミン系硬化剤アルキル化ジアミノジフェニルメタン、（c）エポキシ基を有するポリブタジエン化合物、（d）エポキシ基、アミノ基、メルカプト基の群から選ばれる1個以上の官能基を分子内に有するシランカップリング剤、及び（e）下記に示す特定の粒度分布を有する無機充填材を主成分とする液状封止材料において、各成分の配合割合が重量比で（c）／{（a）＋（b）＋（c）}＝0．03～0．10、（d）／{（a）＋（b）＋（c）}＝0．02～0．10で、かつ（e）／{（a）＋（b）＋（c）＋（d）＋（e）}＝0．50～0．80であることを特徴とする液状封止材料。

【請求項2】（e）無機充填材が、平均粒径が3～10μmで、粒径1μm以下のものが全無機充填材成分中6～45重量%で、かつ粒径30μm以上のものが全無機充填材成分中の25重量%以下の粒度分布を有する請求項1記載の液状封止材料。

【発明の詳細な説明】

【0001】

【発明の属する技術分野】本発明は、半導体の封止に用いられる液状封止材料に関するものである。

【0002】

【従来の技術】プラスチックピングリッドアレイ（以下、PPGAという）型半導体封止には液状の封止材料が用いられているが、セラミックスによる気密封止型に比べて信頼性の点で充分ではなく、デュアルインライン（以下、DIPという）型に比べプラスチックパッケージの普及が遅れていた。PPGA型半導体の信頼性低下の原因としては、［❶パッケージ加工された有機のプリント配線基板から湿気が侵入する。❷DIP型パッケージのトランスファーモールド成形と異なり、無圧下で液状封止材料をパッケージ内に流入し成形するため樹脂中に気泡が残存して、熱ストレスが加わった際にクラックが発生する。❸樹脂と半導体チップ、有機基板との線膨張係数が異なるために熱ストレスが加わった際、界面での剥離を生じ湿気の侵入を容易にしてしまう。］等が挙げられる。

【0003】

【発明が解決しようとする課題】本発明は、プレッシャークッカーテスト（以下、PCTという）や冷熱サイクルテスト（以下、T／Cという）等の促進試験においても半導体の信頼性を大幅に向上できる液状の封止材料を提供するものである。

【0004】

【課題を解決するための手段】そこで本発明は、従来のこのような問題を解決するために鋭意検討を重ねてきた結果、液状エポキシ樹脂、常温で液体である芳香族アミン系硬化剤アルキル化ジアミノジフェニルメタン、エポキシ基を有するポリブタジエン化合物、シランカップリング剤に、特定の粒度分布を有する無機充填材を配合した組成物が、プレッシャークッカーテスト（以下、PCTという）や冷熱サイクルテスト（以下、T／Cという）等の促進試験においても半導体の信頼性を大幅に向上できる封止材料となることを見いだし、本発明を完成するに至ったものである。即ち本発明は、（a）液状エポキシ樹脂、（b）常温で液体である芳香族アミン系硬化剤アルキル化ジアミノジフェニルメタン、（c）エポキシ基を有するポリブタジエン化合物、（d）エポキシ基、アミノ基、メルカプト基の群から選ばれる1個以上の官能基を分子内に有するシランカップリング剤、及び（e）特定の粒度分布を有する無機充填材を主成分とする液状封止材料において、各成分の配合割合が重量比で（c）／{（a）＋（b）＋（c）}＝0．03～0．10、（d）／{（a）＋（b）＋（c）}＝0．02～0．10で、かつ（e）／{（a）＋（b）＋（c）＋（d）＋（e）}＝0．50～0．80であり、（e）の無機充填材はその平均粒径が3～10μmで、粒径1μm以下のものが全無機充填材成分中6～45重量%で、かつ粒径30μm以上のものが全無機充填材成分中の25重量%以下の粒度分布を有する無機充填材を配合した液状封止材料であり、有機プリント配線基板を用いたPPGA型半導体の信頼性を大幅に向上させることができる。

【0005】

【発明の実施の形態】本発明に用いられる（a）の液状エポキシ樹脂は、その成分の50重量%以上は、25℃における粘度が10Pa・s以下であることが好ましい。エポキシ樹脂成分の50重量%以上が低粘度の液状エポキシでないと組成物の粘度が高くなり、PPGAパッケージ中を液状封止材料で流入封止する際、気泡を巻き込んだり、コーナー端部への充填不良が発生し易くなり信頼性低下につながるので好ましくない。エポキシ樹脂の粘度測定方法としては、室温で液状の材料の場合、25℃において東機産業（株）製E型粘度計で測定する。この要件を満足するエポキシ樹脂であれば、特に限定されるものではないが具体例を挙げると、ビスフェノールAジグリシジルエーテル型エポキシ樹脂、ビスフェノールFジグリシジルエーテル型エポキシ樹脂、ビスフェノールSジグリシジルエーテル型エポキシ樹脂、3，3’，5，5’－テトラメチル－4，4’－ジヒドロキシビフェニルジグリシジルエーテル型エポキシ樹脂、4，4’－ジヒドロキシビフェニルジグリシジルエーテル型エポキシ樹脂、1，6－ジヒドロキシビフェニルジグリシジルエーテル型エポキシ樹脂、フェノールノボラック型エポキシ樹脂、臭素型クレゾールノボラック型エポキシ樹脂、ビスフェノールDジグリシジルエーテル型エポキシ樹脂等がある。これらは単独でも混合しても差し支えない。また、信頼性の優れた液状封止材料を得る

ために、使用に耐えるエポキシ樹脂はNa^+、Cl^-等のイオン性不純物はできるだけ少ないものが好ましい。

【0006】本発明に用いられる（b）の芳香族アミン系硬化剤は、アルキル化ジアミノジフェニルメタンであり、常温で液体のものである。芳香環を有さないアミン類は耐熱性に乏しく、零度以下の雰囲気下でも反応性に富むため保存性に劣るという致命的な欠点を有し本発明に適さない。また、信頼性の優れた液状封止材料を得るために、使用に耐えるアミン系硬化剤はNa^+、Cl^-等のイオン性不純物はできるだけ少ないものが好ましい。（b）の芳香族アミン系硬化剤は（a）液状エポキシ樹脂との組み合わせによって、非常に流動性が良い材料を提供することができる。無圧下でパッケージ内に流入し硬化させても、気泡が残らず、ボイド・未充填など流動性の不具合も発生しにくい。主剤である（a）のエポキシ樹脂と、硬化剤である（b）の芳香族アミン系硬化剤アルキル化ジアミノジフェニルメタンとの配合モル比｛（a）／（b）｝は0．9～1．2が望ましい。0．9未満の、硬化剤が過多の場合は、過剰に未反応のアミノ基が残存することとなり、耐湿性の低下・信頼性の低下に繋がる。逆に1．2超えると即ちエポキシ樹脂が多くなると硬化が不十分となり、信頼性の低下に繋がる。

【0007】本発明に用いられるエラストマーとしては、（a）のエポキシ樹脂との相溶性が良く、低応力化及び強靭化が期待される（c）のエポキシ基を有するポリブタジエン化合物が挙げられる。一般にエラストマーは、エポキシ樹脂との相溶性に欠けるため注入硬化した後はブリードのため成形性が低下する性質を有する。しかし、エポキシ基を分子の一部に組み込むことにより相溶性が増し、硬化剤（b）と一部反応し架橋するため、ブリード性は良くなり、エポキシ基を有するポリブタジエン特有の低応力化及び強靭化も発現できると考えられる。エポキシ基を有するポリブタジエン化合物は、数平均分子量が1000～2000が好ましい。1000未満だとブリードし易くなり、2000を越えると粘度が高くなり、いずれも好ましくない。また、エポキシ含有率（主鎖付加モル分率%）は、3～10%が好ましい。3%未満だと相溶性に欠け、10%を越えると硬化剤と架橋し、いわゆる海島構造を取らなくなるため低応力化が望めなくなる。低応力化の確認には例えば3点曲げ試験、強靭化の確認には例えばKIC測定が挙げられるが、いずれのテストの結果でも優れた結果を得ることができる。このエポキシ基を有するポリブタジエン化合物は、その添加量を調整することにより、低応力性及び靭性を最大限に引き出すことができる。添加量は、（c）／｛（a）＋（b）＋（c）｝＝0．03～0．10が望ましいが、0．03未満だと低応力化及び強靭化の効果が望めなく、特にT／C（温度サイクルテスト）時に表面クラックが発生し信頼性の不良に繋がる原因となる。また、0．10を越えると（a）のエポキシ樹脂との相溶性が悪くなりパッケージ表面に油浮き、ブリードするといった成形性低下の原因となる。また、更に低応力効果があり、かつ（c）のエポキシ基を有するポリブタジエン化合物と相溶性のある、ランダム共重合シリコーン変性エポキシ樹脂、ランダム共重合シリコーン変性フェノール樹脂、又はエポキシ基含有のポリオレフィン等と組み合わせても良い。

【0008】（d）のエポキシ基、アミノ基、メルカプト基の群から選ばれる1個以上の官能基を分子内に有するシランカップリング剤としては、エポキシシラン（例えば、信越化学工業(株)製KBM－403）が好ましい。また用途に応じて基板との密着性を高めたい場合には、必要に応じてアミノシランおよびメルカプトシランをカップリング剤全量に対し一部ないし全部添加してもよい。

【0009】（e）の無機充填材（以下単に充填材という）としては、例えば、結晶シリカ、溶融シリカ等が用いられる。形状は一般に球状、破砕状、フレーク状等があるが、充填材をより多く添加することにより線膨張係数の低減化が図られ、その効果を上げるためには球状の無機充填材が最も良い。添加量は、（e）／｛（a）＋（b）＋（c）＋（d）＋（e）｝＝0．50～0．80が望ましい。0．50未満だと、上述の線膨張係数の低減効果は小さく、0．80を越えると結果として得られる液状封止材料の粘度が高くなり過ぎ、実用レベルではないため好ましくない。また充填材の粒度分布を調整することにより粘度等の流動特性を最大限に引き出すことが可能である。一般に分布範囲の広い粒度分布をもつ充填材ほど、大きな粒径をもつ充填材ほど粘度が低くなる傾向があることが知られている。しかし、低粘度化を目的に例えば50μm以上の大きな粒径だけを揃えた充填材は、確実に粘度は低くなるものの、硬化中に比重の比較的重い充填材が沈み、硬化物の上下で組成比率の異なる、いわゆるフィラー沈降が発生する。また、粒径の大きな充填材を使う欠点として、狭い隙間に流入しないという点が挙げられる。PPGA型パッケージに代表されるように、多ピン化省スペース化のパッケージの傾向にあって、一例としてワイヤー・ワイヤー間のピッチが最近狭くなってきている。このような傾向にあり無圧下で液状封止材料を流入し、ボイド・未充填など流動性の不具合がないよう成形するために、充填材の粒径を小さくしなければならない。しかし粒径を小さくすることによって流動性が損なわれる不具合も多くなる。そこで充填材の平均粒径を3～10μmと、従来の液状封止材料のそれより小さくし、かつ粒径30μm以上のものが全充填材成分中の25重量%以下と粒径を小さくすることにより、流動性も損なわない。また1μm以下のものが全充填材成分中6～45重量%と、微粒の充填材を適量入れ、粒度分布を調整することで、硬化時に微粒の充填

材が沈みやすい充填材の沈降を抑えることができる。本発明でいう粒度分布および平均粒径は、レーザー式（Horiba, LA-500）にて測定する。なお平均粒径は、メジアン径とした。本発明の液状封止材料材料には、前記の必須成分の他に必要に応じて他の樹脂や反応を促進するための触媒、希釈剤、顔料、カップリング剤、難燃剤、レ＊

＊ベリング剤、消泡剤等の添加物用いても差し支えない。液状封止材料は、例えば各成分、添加物等を３本ロールにて分散混練し真空下脱泡処理して製造する。

【００１０】

【実施例】以下本発明を以下に示す実施例及び比較例で説明する。

・ビスフェノールＦジグリシジルエーテル型エポキシ樹脂：
（エポキシ当量１５５、１．６Ｐａ・ｓ／２５℃）　１００重量部
・ナフタレンＦジグリシジルエーテル型エポキシ樹脂：
（当量１３５、１２４Ｐａ・ｓ以下／２５℃）
・アルキル化ジアミノジフェニルメタン硬化剤：
（アミノ当量６５）　４２重量部
・エポキシ基を有するポリブタジエンゴム：　５重量部
（数平均分子量１５００、エポキシ含有率５モル％）
・グリシジルトリメトキシシラン：　６重量部
・溶融シリカ：　３５０重量部
・カーボンブラック：　１重量部

上記の原材料を３本ロールにて、分散混練し真空下脱泡処理をして液状封止材料を得た。得られた液状封止材料を用いて、ＰＰＧＡパッケージを封止し１６５℃で３時間オーブン中で硬化して半導体パッケージを得た。

【００１１】《評価方法》

・粘度：Ｅ型粘度計（２５℃）にて、２．５ｒｐｍで測定したものを値とした。この値が高いほど悪い。粘度が５０Ｐａ・ｓを越えるとディスペンス時の作業性が悪くなる。

・チキソ比：上述粘度計で、０．５ｒｐｍと２．５ｒｐｍでの粘度の比を値とした。

・保存性：初期粘度の倍の粘度になる時間をとった。○は７２時間以上、△は２４～７２時間、×は２４時間以下

・硬化性：ＰＰＧＡパッケージピースパーツに液状封止材料を注入し、硬化条件１６５℃／３時間にて硬化し、パッケージ表面のボイドの数、フィラー分離を観察し

※た。パッケージ表面のボイドの数は顕微鏡で観察し、数μｍ以上のボイドを家運とした。未充填パッケージは、超音波殺傷機（以下ＳＡＴという）にて観察した。フィラー分離は、パッケージの断面を研磨し、表面の樹脂層の厚みを測定した。５μｍ以上のものをフィラー分離有りとして表した。評価したＰＰＧＡパッケージの数は１０個である。

・硬化後の剥離・クラック

①処理前

②ＰＣＴ処理（１２５℃／２．３ａｔｍ）７２０時間後

③Ｔ／Ｃ処理（－６５℃／３０分←→１５０℃／３０分）１０００サイクル後についてＳＡＴを用いて、半導体チップとプリント基板界面との剥離、クラックの有無を確認した。評価したＰＰＧＡパッケージの数は、１０個である。

【００１２】

表　1

	シリカ					
	A	B	C	D	E	F
平均粒径（μｍ）	5.4	4.2	7.8	2.5	3.2	7.3
１μｍ以下の重量％	30	39	20	40	48	10
１～３０μｍの重量％	55	52	62	55	51	61
３０μｍ以上の重量％	15	9	18	5	1	29

【００１３】

表　2

	実施例				
	1	2	3	4	5
配合（重量部）					
ﾋﾞｽﾌｪﾉｰﾙF型ｼﾞｸﾞﾘｼｼﾞﾙｴｰﾃﾙｴﾎﾟｷｼ樹脂	100	100	100	100	60
ﾅﾌﾀﾚﾝ型ｼﾞｸﾞﾘｼｼﾞﾙｴｰﾃﾙｴﾎﾟｷｼ樹脂					40

アルキル化ジアミノジフェニルメタン		42	42	42	42	47
ポリブタジエンゴム		5	5	5	5	5
グリシジルトリメトキシシラン		6	6	6	6	6
カーボンブラック		1	1	1	1	1
溶融シリカA		350	500			350
溶融シリカB				350		
溶融シリカC					350	
特性						
粘度 (Pa·s)		30	45	36	24	38
チキソ比		1.2	1.2	1.3	1.1	1.3
保存性		○	○	○	○	○
硬化性	ボイドの数	0	0	0	0	0
	未充填	0	0	0	0	0
	フィラー分離	無	無	無	無	無
硬化後	剥離	0	0	0	0	0
	クラック	0	0	0	0	0
PCT処理後	剥離	0	0	0	0	0
	クラック	0	0	0	0	0
T／C処理後	剥離	0	0	0	0	0
	クラック	0	0	0	0	0

【0013】

表 3

		比較例				
		1	2	3	4	5
配合（重量部）						
ﾋﾞｽﾌｪﾉｰﾙF型ｼﾞｸﾞﾘｼｼﾞﾙｴｰﾃﾙｴﾎﾟｷｼ樹脂		100	100	100	100	30
ﾅﾌﾀﾚﾝ型ｼﾞｸﾞﾘｼｼﾞﾙｴｰﾃﾙｴﾎﾟｷｼ樹脂						70
アルキル化ジアミノジフェニルメタン		42	42	42	42	45
ポリブタジエンゴム		5	5	5	5	5
グリシジルトリメトキシシラン		6	6	6	6	6
カーボンブラック		1	1	1	1	1
溶融シリカA					200	350
溶融シリカD		350				
溶融シリカE			350			
溶融シリカF				350		
特性						
粘度 (Pa·s)		43	54	27	17	76
チキソ比		1.1	1.2	1.3	1.1	1.3
保存性		○	○	○	○	×
硬化性	ボイドの数	2	15	0	0	3
	未充填	1	2	0	0	20
	フィラー分離	有	無	有	無	無
硬化後	剥離	0	0	0	0	0
	クラック	0	0	0	0	0
PCT処理後	剥離	0	0	0	10	4
	クラック	0	0	0	6	2
T／C処理後	剥離	0	0	0	10	0
	クラック	0	0	0	10	0

【0014】

＊50＊【発明の効果】本発明の液状封止材料で半導体パッケー

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ジの封止を行うと、プレッシャークッカーテストや冷熱サイクルテストにおいても剥離クラックのない高信頼性の半導体を得ることがでるので工業的メリット大である。

フロントページの続き

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